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Thirteenth day of January 2005

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The Australian National University

A U S T R A L I A

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PROVISIONAL SPECIFICATION

for the invention entitled:

"Water-based cleaning"

The invention is described in the following statement:

WATER-BASED CLEANING

Technical Field

- 5 The present invention relates to the cleaning of articles and surfaces, and is particularly concerned with cleaning using water, optionally with other cleaning agents, for example in combination with other fluids.

Background

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The fundamental reason why oil molecules do not dissolve in water is because hydrocarbon (and fluorocarbon, chloro-hydrocarbon and silicone) molecules are non-polar and so cannot replace the strong water-water bonds, which need to be broken to incorporate the solute molecule, with equally strong water-solute bonds. For hydrocarbon and the like molecules to be dissolved in water, the water molecules have to be forced apart so that they can then form ice-like clusters around the hydrocarbon. The larger the hydrocarbon molecule, the more water molecules need to be disrupted, and so the lower the solubility. For example, heptane is slightly soluble in water but the larger molecule dodecane is almost completely insoluble. Because this disruption of water is unfavoured, two (or more) hydrocarbon molecules in water will experience a short-range attractive force, caused by the favoured release of any disrupted water molecules back into their bulk state. Hydrocarbon molecules are, therefore, forced together and 'bond' in water. This bond is called the hydrophobic bond (1). The same factors explain why polar materials, such as sugars, alcohol and salts, are readily soluble in water, since these solutes interact favourably with the surrounding water molecules.

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However, molecular solutions are not the only state for mixing phases. In nature many insoluble materials are 'dispersed' in water in a finely divided form, as a colloidal solution, such as biological cells in blood, clay particles in river water and oil/water emulsions. In each case, microscopic particles of one phase are stabilized in water,

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usually by repulsive electrostatic forces, which can overcome the ubiquitous attractive van der Waals force (2). Over twenty years ago another important, attractive force was discovered, acting between hydrophobic particles in water. This force was called the long range hydrophobic interaction (3). The unexpected strength and range of this force has made a proper theoretical explanation difficult, although it is suggested that this force is a cause of instability of hydrophobic colloids in water (4). In the last few years experimental studies have provided evidence in support of an explanation related to the presence of dissolved gas in water (4,5,6). Even in some early studies (7) there was experimental evidence for the formation of vapour- or gas-filled bridges created as two hydrophobic surfaces were separated in water. Further evidence for this effect was obtained recently in a study of the effect of complete de-gassing on the dispersion of oil droplets (and fine Teflon powder) in water (8). De-gassing appears to facilitate the dispersion of oils and finely divided hydrophobic solids, without the need for common dispersants, such as polymers and surfactants. However, gassing levels do not appear to affect the stability of the emulsions, once formed (8, 9).

Water-based cleaning is effective because hydrophilic, polar solutes, such as sugar and salt (ie 'dirt') dissolve readily in water, which is a good general purpose solvent. However, hydrophobic dirt, such as charcoal, grease and oil, is not water soluble at normal temperatures. To overcome this problem, these materials are commonly dispersed in water via a combination of mechanical agitation (during conventional washing) and by the use of added surface active solutes, such as soaps or detergents (surfactants), which coat hydrophobic materials in water. Surfactant molecules adsorb onto hydrophobic surfaces in water, making them hydrophilic which enhances dispersion (not solubility) in water, so that they can be carried away in the aqueous phase during cleaning. Mechanical agitation is a vital component of conventional cleaning. Liquid hydrocarbon oils can also be absorbed into micelles formed by these surfactants, facilitating cleaning.

Summary of the Invention

It would be highly advantageous to be able to remove hydrophobic dirt from articles and surfaces using water without any or with reduced amounts of surfactants and
5 other dispersants.

According to the present invention, there is provided a method of cleaning an article or surface with water, which comprises applying de-gassed water to the article or surface whereby dirt on the article or surface disperses or dissolves in the water.

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Also according to the present invention, there is provided apparatus for cleaning an article or surface with water, which comprises means for degassing the water and means for applying the de-gassed water to the article or surface whereby dirt on the article or surface disperses or dissolves in water.

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The relatively low level of dissolved gas present in water at room temperature, of about 1mM (or 20mL of gas per litre) suggests that its influence should be limited to processes involving relatively low (hydrophobic) surface areas. Thus, for micellar
(10) solutions and microemulsions (11), in which the number of dissolved gas
20 molecules is small relative to the interfacial area available per unit volume of mixture, de-gassing appears not to influence the properties of these systems.

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By comparison, the breakaway of oil droplets from a macroscopic oil/water interface, and the dispersion of finely divided hydrophobic particles, offers a low surface area process which can be influenced by a reduction of this relatively low level of dissolved gas. This is even more the case when dissolved gas molecules accumulate next to oil-water (and hydrophobic particle/water) interfaces. This is believed to be because dissolved oxygen and nitrogen (dissolved carbon dioxide is at the much lower level of about 10 μ M) molecules, like hydrocarbons, will disrupt adjacent water
30 molecules because of their non-polar nature and weak van der Waals interaction with water. The presence of macroscopic, hydrophobic surfaces ought to attract these

- dissolved gas molecules from the water phase and this accumulation may also be aided by the increased gas solubility in hydrocarbon oils, which can be an order of magnitude higher than water. The presence of this layer of dissolved gas, in a thin film, which is placed under a negative (suction) pressure during droplet/particle breakaway, may cause gas cavities to nucleate, which will create a bridge between the surfaces and oppose droplet release. Vapour cavitation is expected for the separation of hydrophobic surfaces in water (12). The precise detail of this process is not known but cavity bridging between the surfaces and an enhanced van der Waals attraction between the surfaces will both act to hold the surfaces together. Whatever the mechanism, reducing the amount of dissolved gas in the water has been found to reduce the forces holding the oil and other hydrophobic particles (eg oil, grease and charcoal, and herein separately or together referred to as "hydrophobic dirt") to the article or surface and to allow the hydrophobic dirt to be released into the water.
- Using de-gassed water to aid in the dispersive removal of hydrophobic (solid or liquid) dirt represents an entirely different approach compared to cleaning with detergents. The main detergent action is to coat hydrophobic surfaces to make them hydrophilic, and hence readily dispersible in water. However, in both cases the crucial step will involve the separation of two surfaces from intimate molecular contact and the exposure of a least one hydrophobic surface to water. This will occur even in the presence of detergent, just prior to its adsorption. Simple thermodynamic arguments predict that the separation of one or two hydrophobic surfaces in water is expected to produce cavitation between the surfaces. As discussed above, this cavitation acts to prevent the separation, and hence removal of dirt, both because of the energy needed to vaporise water and the strong, short-range van der Waals force generated between two materials across a vapour phase.

In detergent cleaning, hydrophobic materials usually become charged due to detergent adsorption and this helps to stabilise them. However, it has recently been demonstrated that hydrophobic colloids naturally develop a significant charge in water which also helps stabilise them in water (13). In detergent cleaning, the

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surfactant-coated hydrophobic dirt is thermodynamically more stable in water than hydrophobic dirt dispersed under de-gassed conditions. However, we have demonstrated that, although not thermodynamically stable in water, hydrocarbon oil droplets, dispersed using de-gassed conditions, do not coalesce and remain in a meta-
5 stable state of more than sufficient duration to be effective in cleaning.

By "applying the de-gassed water" as used herein is meant any arrangement by which the de-gassed water can be caused to act on the article or surface in the method or apparatus of the invention. This includes introducing an article to a container of the
10 de-gassed water in which the article may be left for a period of time to "soak", with or without agitation. It also includes spraying or blasting the article or surface with the de-gassed water, preferably using an airless pump, and merely causing the de-gassed water to relatively flow over the article or surface.

15 The invention described herein is therefore analogous in some respects to normal cleaning, except that the dispersion of hydrophobic dirt is achieved at least primarily, or in some embodiments at least in part, by the use of de-gassed water. The dispersion of hydrophobic dirt, including the time taken for the cleaning, is advantageously enhanced by the use of mechanical action combined with de-gassed
20 water. This mechanical action can be in the form of, for example, jets of de-gassed water, preferably fine jets, directed onto a dirty article or surface, or any conventional mechanical action. Mechanical action combined with the dispersive power of de-gassed water will disperse hydrophobic dirt, while hydrophilic, polar, dirt (eg salts, sugars) will be dissolved in the normal manner. Thus, soluble dirt is dissolved, while
25 hydrophobic dirt is dispersed and all of the dirt may then be rinsed away. Long term stability of the dispersion of dirt in water is not required in cleaning, and subsequent de-stabilisation could actually be useful. However, as with conventional cleaning, the addition of hydrophilic, polymeric stabilisers, such as sodium carboxymethylcellulose, may also be used to enhance the longer term dispersive
30 power of de-gassed water, preventing the re-deposition of the dirt.

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By "de-gassed water" is meant that at least 90%, preferably at least 97%, of the dissolved gases that are present in the source water are removed. The cleaning action of the de-gassed water will be enhanced at higher levels of de-gassing, and more preferably at least about 99.99%, most preferably about 99.999%, of the dissolved gases are removed from the source water. The source water may be distilled water, tap water or, for some purposes, even recycled cleaning water.

The de-gassing of the water can be achieved by any suitable vacuum pump with a nitrogen trap. In one embodiment, de-gassing is achieved by repeated freezing and pumping using an efficient mechanical pump. Once the space above the frozen water was out-gassed, to typically better than a mTorr, a Teflon tap was closed and the water warmed to room temperature so that remaining dissolved gases were pulled into the space above the liquid. This may be repeated, for example, up to four or five times to ensure almost complete removal of the dissolved gas. When connected to a separate vacuum line, of substantially greater volume, the mechanical pump achieved pressures down to 20 – 40 μ Torr. Evacuation of the water to lower than a mTorr corresponds to greater than 99.999% removal of the dissolved gas. Evacuation of the water to lower than about 20 Torr corresponds to greater than about 97% removal of dissolved gas, and evacuation of the water to lower than about 20 milliTorr corresponds to greater than about 99.99% removal of dissolved gas.

Alternatively, the water may be de-gassed by any other suitable method. For example, water can be de-gassed to the required level using a hydrophobic porous membrane (14, 15).

The cleaning may be performed at any temperature between (not including) 0°C and 100°C, but is conveniently performed at room or ambient temperature.

The potential advantages of a detergent-free cleaning system are enormous in terms of cost and environmental savings, and might be of particular value for specialist applications. Some examples follow.

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Micro-electronic circuits currently have to be cleaned with relatively toxic solvents that are expensive and have to be recycled. De-gassed water can be sprayed onto delicate electronic devices without the disadvantage of leaving residual detergent
5 coatings. The washings can be discarded.

Automobile surfaces, and other surfaces, may be cleaned using a tube held close to the contours of the surface and moved across the surface. Holes in the tube produce fine jets of de-gassed water, which hit the surface and clean via dissolution and
10 dispersion.

Household clothes' washing systems may be developed using agitation of clothes in a basin with fine jets of de-gassed water covering all articles of clothing over the period of agitation. Clothes and other articles may also be left to soak in a container of de-
15 gassed water optionally with agitation of the articles.

Vegetables are often cleaned using a water-based flotation process. De-gassed spraying could offer a detergent-free alternative.

20 The rate of diffusion of air into de-gassed water is remarkably slow and so should not present a problem for spray processes, where the de-gassed water is exposed to air for only a brief length of time (ie. seconds). Theoretically, at room temperature it takes about 10 days to reach dissolved gas saturation to a depth of 1cm in quiescent, de-gassed water. However, external factors, including vibration and convection, may
25 accelerate the diffusion process.

According to a further aspect of the invention, it has been found that the cleaning process using de-gassed water may be substantially enhanced by first dissolving hydrophobic dirt on the article using a de-gassed non-aqueous solvent.

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- This two-stage cleaning process is based on the solvent properties of non-aqueous solvent for hydrophobic dirt and the solvent properties of water for polar dirt, combined with the enhanced dispersive powers of de-gassed water and de-gassed solvent. Hydrophobic dirt (eg oils, grease) will readily dissolve in the de-gassed solvent in the first stage and hydrophilic, polar, dirt (eg salts, sugars) will dissolve in the second stage water wash. In addition, the solvent will be readily dispersed in subsequent (de-gassed) aqueous washes and hence the solvent and dirt will be completely removed. The solvent and water can be subsequently phase separated and recycled after suitable cleaning. Using de-gassed water to remove de-gassed solvent represents an entirely different approach to cleaning without detergents. This cleaning process will be of particular value in applications where detergent residues are not acceptable, such as in the preparation of silicon wafers and in the cleaning of surgical equipment.
- 15 The non-aqueous solvent is advantageously hydrophobic. Possible non-aqueous solvents include hydrocarbons, fluorocarbons, chloro-hydrocarbons and silicone liquids. Some examples are dodecane, squalene, hexamethyldisiloxane and perfluorohexane.
- 20 By de-gassed non-aqueous solvent is meant that at least 90%, preferably at least 97% of the dissolved gasses present in the source solvent are removed. The dissolving action of the de-gassed non-aqueous solvent will be enhanced at higher levels of de-gassing, for example if up to about 99.99%, or even up to about 99.999%, of the dissolved gases are removed from the source solvent.
- 25 De-gassing of the non-aqueous solvent may be performed by the same multiple freeze/thaw/pumping cycles as described above for the de-gassed water. Alternatively, the water and/or non-aqueous solvent may be de-gassed in a vacuum tower. In that regard, vacuum towers have been used commercially to de-gas liquids.
- 30 It is noted that it is unlikely that membranes will be used for solvent de-gassing.

Brief Description of the Drawings

Aspects of the present invention will now be described in detail, by way of example only, with reference to the accompanying drawings, in which:

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Figure 1 is graph showing percentage of de-gassing against vacuum pressure in a mechanical pump with a liquid nitrogen trap;

Figures 2a and 2b are photographs showing samples as described in Example 1;

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Figure 3 is a graph illustrating the turbidity of normal gassed water and of de-gassed water after shaking in a container contaminated with dodecane as described in Example 2;

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Figure 4 is a graph illustrating the turbidity of water washings produced on washing hexamethyldisiloxane from Pyrex glassware as described in Example 3;

Figure 5 is a graph illustrating the turbidity of water washings produced on washing perfluorohexane from Pyrex glassware as described in Example 4;

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Figure 6 is a photograph showing samples one minute after shaking, as described in Example 4; and

Figure 7 is a schematic representation of one form of cleaning apparatus.

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Figure 1 illustrates the vacuum required for a degree of de-gassing between 99.87% and 99.999%, if it is assumed that the final pressure achieved on several cycles of freeze/thaw/pumping is given by the pressure in equilibrium with the final frozen liquid, which on being melted does not give any visible bubbling/out-gassing.

30

Example 1

Distilled water was produced from tap water via a sequential process of coarse filtration, activated charcoal filtration, reverse osmosis filtration and, finally,
5 distillation into a glass storage vessel housed in a laminar flow, clean air cabinet. All the chemicals used were of the purest grade available and used as purchased.

Samples of clean, distilled water were out-gassed by a process of repeated freezing in liquid nitrogen, followed by pumping down to a pressure of 0.01mbar and then
10 melting in a sealed tube. The dissolved gas produced on each melting cycle was removed on re-freezing. Although this process was carried out five times, typically no further de-gassing on melting was observed after 3-4 cycles. The vacuum pressure of 0.01mbar corresponds to a de-gassing level of about 99.999%.

15 This water was then used to clean strips of standard filter paper having finely divided activated charcoal rubbed into their surface to produce a uniform blackened region, by placing each strip into a respective test tube and pouring the water into the tube. The cleaning effect of the de-gassed water was compared with that of distilled water that had not been de-gassed.

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In Figure 2a the left-hand tube contains the de-gassed water and the right-hand tube the non de-gassed distilled water. In both cases the same volume of water was simply poured onto the dirty paper.

25 In Figure 2b the left-hand tube contains the non de-gassed distilled water and the right-hand tube the de-gassed water. In both cases the same volume of water was poured onto the dirty paper and then the tubes with the strips immersed in the water were vigorously shaken by hand for 8 seconds.

30 In both of these rudimentary, non-optimum, cleaning experiments it was immediately obvious from visual examination that the de-gassed water removed substantially

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greater amounts of the activated charcoal. In the experiment whose results are illustrated in Figure 2a, in pouring the de-gassed water it was clear that some areas were being cleaned and a significant amount of fine carbon was carried to the surface. By comparison, in the experiment whose results are illustrated in Figure 2b, on shaking the tube, the de-gassed water produced significantly more charcoal sediment and a more cloudy solution.

It is interesting that these simple experiments clearly indicate that de-gassed water does have an improved cleaning effect because the substrate in this case, paper, is hydrophilic and finely divided activated charcoal is, in any case, fairly easily dispersed in normal, gassed water.

However, further studies indicate that the buoyancy of porous powders, such as activated charcoal, may be a factor in determining the ability of gassed or de-gassed water to 'float' off and hence clean. Caution is therefore required in interpreting these observations. In addition, most hydrophobic solids have water contact angles close to but less than 90° and so cavitation effects are somewhat dependent on surface heterogeneity. Hydrophobic liquids are not susceptible to these effects and hence give an unambiguous demonstration of the effect of de-gassing, as will be seen in the following examples.

Example 2

In this example, a small amount of the hydrocarbon oil dodecane was left in the base of each of two glass tubes. The same volume of normal water that had not been de-gassed and water that had been de-gassed in the manner described in Example 1 was poured into respective tubes and the tubes were shaken vigorously for 8 seconds.

Figure 3 shows the turbidity of the water in each tube for five minutes after this procedure. The results clearly demonstrate that de-gassed water is more effective at removing residual oil 'dirt' on glass. Similar results were achieved with the

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hydrocarbon oil squalene. These results are particularly interesting and important because the oil was completely equilibrated with the atmosphere prior to cleaning and hence contained dissolved gas at a significantly higher level than even the normal water. The diffusion of dissolved gas from the oil does not appear to prevent the
5 cleaning enhancement of de-gassed water. Presumably this is rate dependent and rapid cleaning will favour the enhancement using de-gassed water.

Further cleaning experiments were carried out on hexamethyldisiloxane (Example 3) and perfluorohexane (Example 4) in Pyrex glassware. Typically a small, known
10 amount of the non-aqueous solvent was poured into the bottom of a glass tube and either ordinary distilled water or de-gassed water was introduced, the tube sealed and vigorously shaken (typically for 8secs) and the resultant water phase turbidity measured with time. In some experiments the non-aqueous solvent was also de-gassed. All water transfers were carried out in laminar filtered air cabinets.

15

In Examples 3 and 4, the de-gassed water was prepared in the manner described in Example 1, and the de-gassed non-aqueous solvent was prepared by the same procedure.

20 **Example 3**

This example illustrates the embodiment of the cleaning process of the invention using both de-gassed water and de-gassed non-aqueous solvent, hexamethyldisiloxane and compares it with the use of only de-gassed water and with cleaning using non de-
25 gassed water and non de-gassed solvent.

In these rudimentary cleaning experiments with hexamethyldisiloxane, it was clear from visual examination that the de-gassed water removed the gassed, non-aqueous solvent more effectively than distilled water. However, de-gassing the solvent as well
30 as the water produces a substantial enhancement in dispersion. In order to quantify

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these observations, measurements were obtained for the turbidity of water washings produced on washing hexamethyldisiloxane from Pyrex glassware.

Figure 4 illustrates the turbidity measurements over 65 minutes, with "blank" showing the experiment in which neither the water nor the solvent were de-gassed.

Example 4

This example illustrates the embodiment of the cleaning process of the invention using both de-gassed water and de-gassed perfluorohexane and compares it with cleaning using non de-gassed water and non de-gassed solvent. Again, the performance was assessed by using turbidity measurements.

The results are shown in Figure 5, from which it is clear that the ability of rinsing water to disperse the perfluorohexane, and hence clean, is significantly enhanced by de-gassing the water and the solvent. Even within a minute after shaking, the non de-gassed liquids are almost completely phase separated, whereas the de-gassed liquids form a very stable emulsion, as shown in the photographs in Figure 6. Washing the Pyrex tube with de-gassed water after the tube has been emptied will completely remove the (de-gassed) fluorocarbon solvent.

The results presented in Examples 3 and 4 indicate that a two-stage cleaning system of de-gassed solvent followed by de-gassed water rinsing may offer an even more effective alternative to detergent based cleaning than merely using de-gassed water. The system may be particularly useful for applications where detergent residues need to be avoided, for example, in silicon wafer manufacture and surgical equipment cleaning. De-gassing of the oil appears to have a substantial effect on the inhibition of cavity formation, and hence supports oil dispersion. This indicates that, in the absence of degassing of the oil, the higher solubility of gases in the oil phase provides a reservoir of gas which can diffuse into the aqueous phase, enhancing the cavitation

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process as droplets start to separate. Removal of this dissolved gas from the oil allows much more effective droplet dispersion.

It will be appreciated that the de-gassed water will re-equilibrate on exposure to the atmosphere causing the level of dissolved gasses to increase. Therefore, the time of exposure of the de-gassed water to the atmosphere prior to dispersion is advantageously minimised. A suggested cleaning system is illustrated in Figure 7. In the cleaning method of the invention, it will be preferred to both reduce exposure time and supply mechanical action to aid dispersion. In the case illustrated in Figure 7, the mechanical action is supplied as liquid spray pressure and momentum. The sprayed liquid may be only de-gassed water. However, since it appears that de-gassed oil is more effectively dispersed by de-gassed water than gassed oil, sequential spray cleaning based on de-gassed oil rapidly followed by de-gassed water rinsing may offer an effective detergent-free cleaning solution. The de-gassed oil could be a hydrocarbon, fluorocarbon, chloro-hydrocarbon or silicone liquid. This type of system offers effective detergent-free cleaning which should disperse and remove all hydrophobic and hydrophilic forms of dirt.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope. The invention also includes all the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

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Throughout this specification, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be

25 understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

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The reference to any prior art in this specification is not, and should not be taken as, an acknowledgment or any form of suggestion that that prior art forms part of the common general knowledge in Australia.

5 Dated this 16th day of August 2004

The Australian National University

By Its Patent Attorneys

DAVIES COLLISON CAVE

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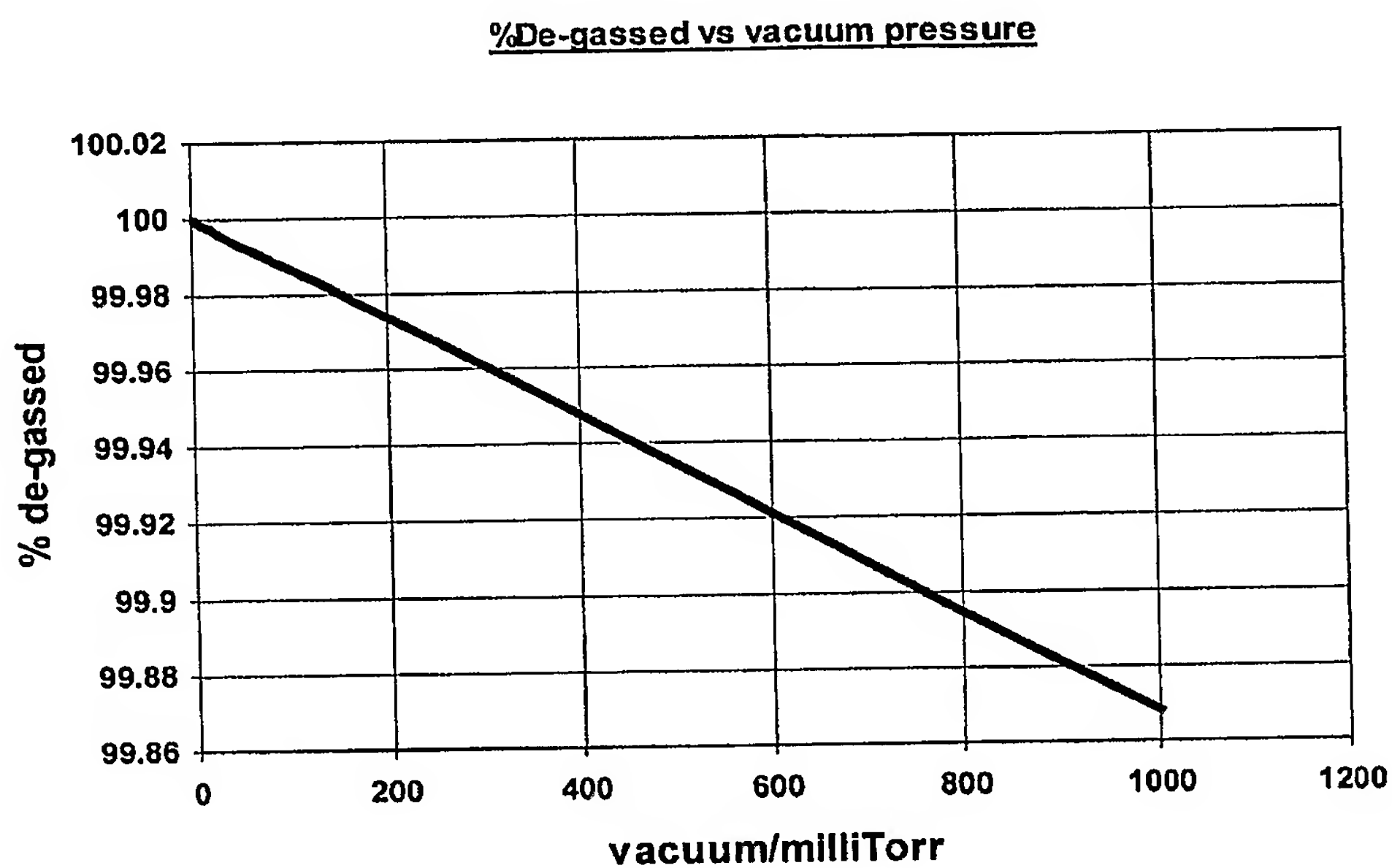


Figure 1

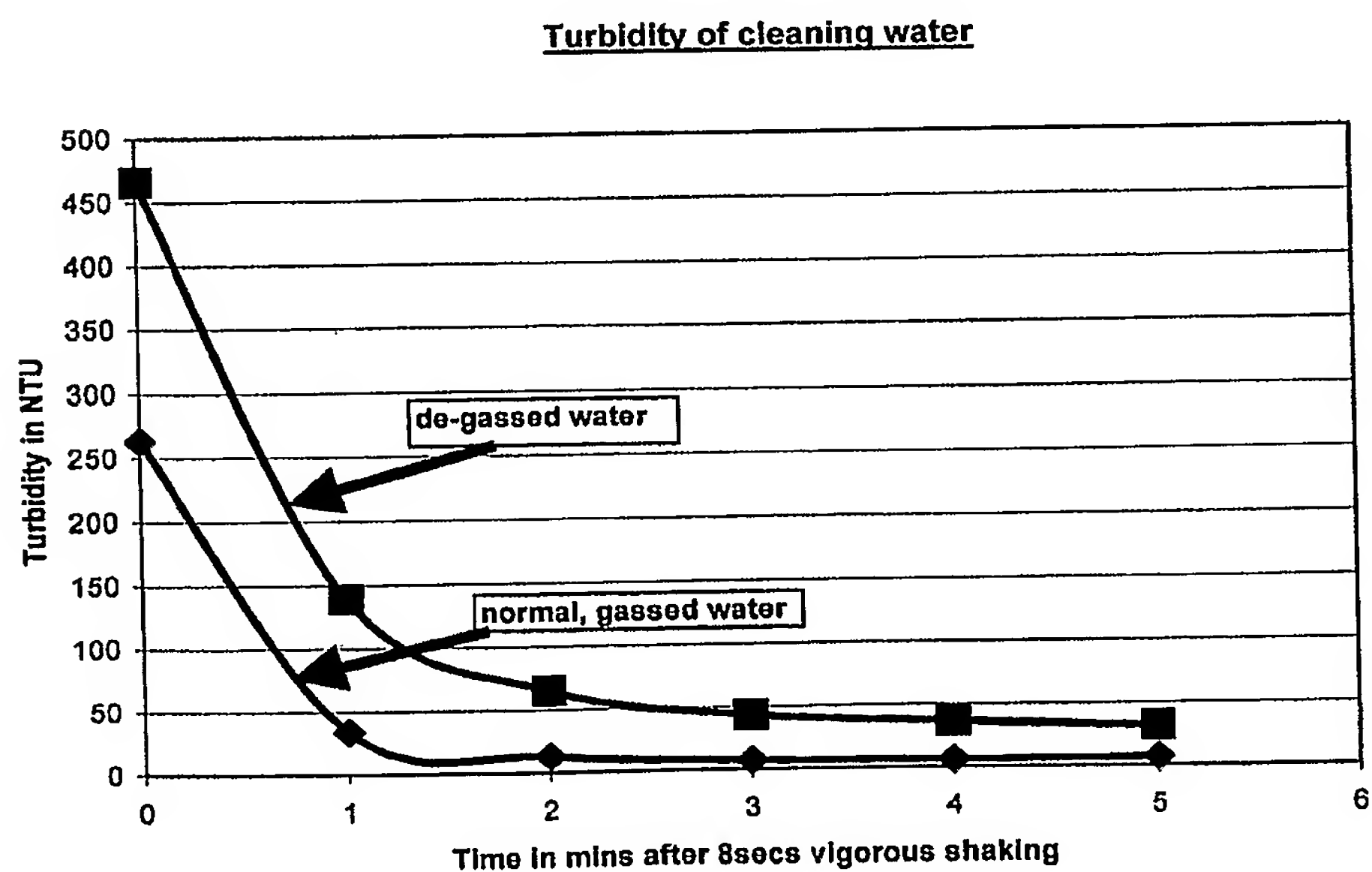


Figure 3

- 2/6 -

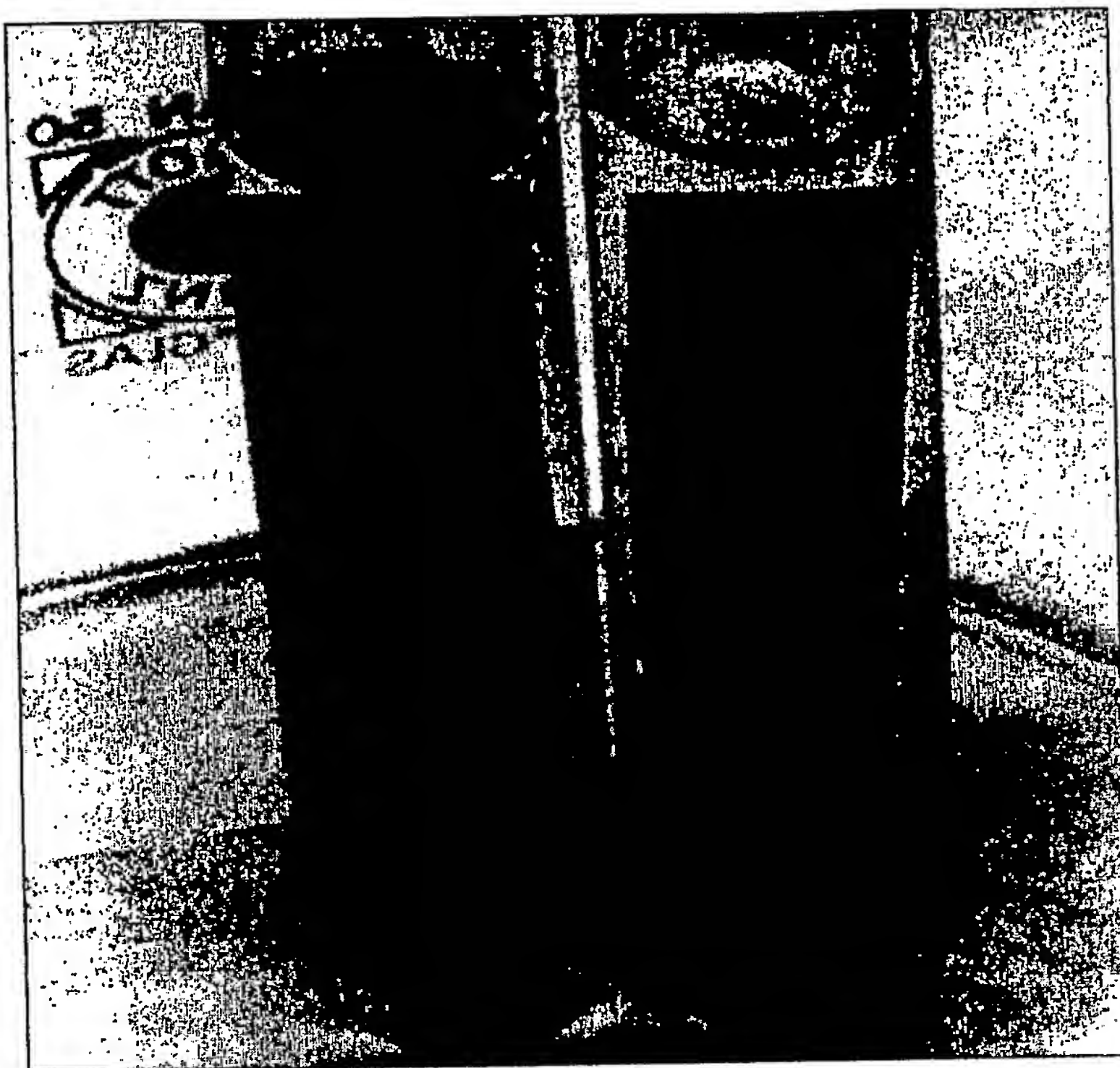


Figure 2a

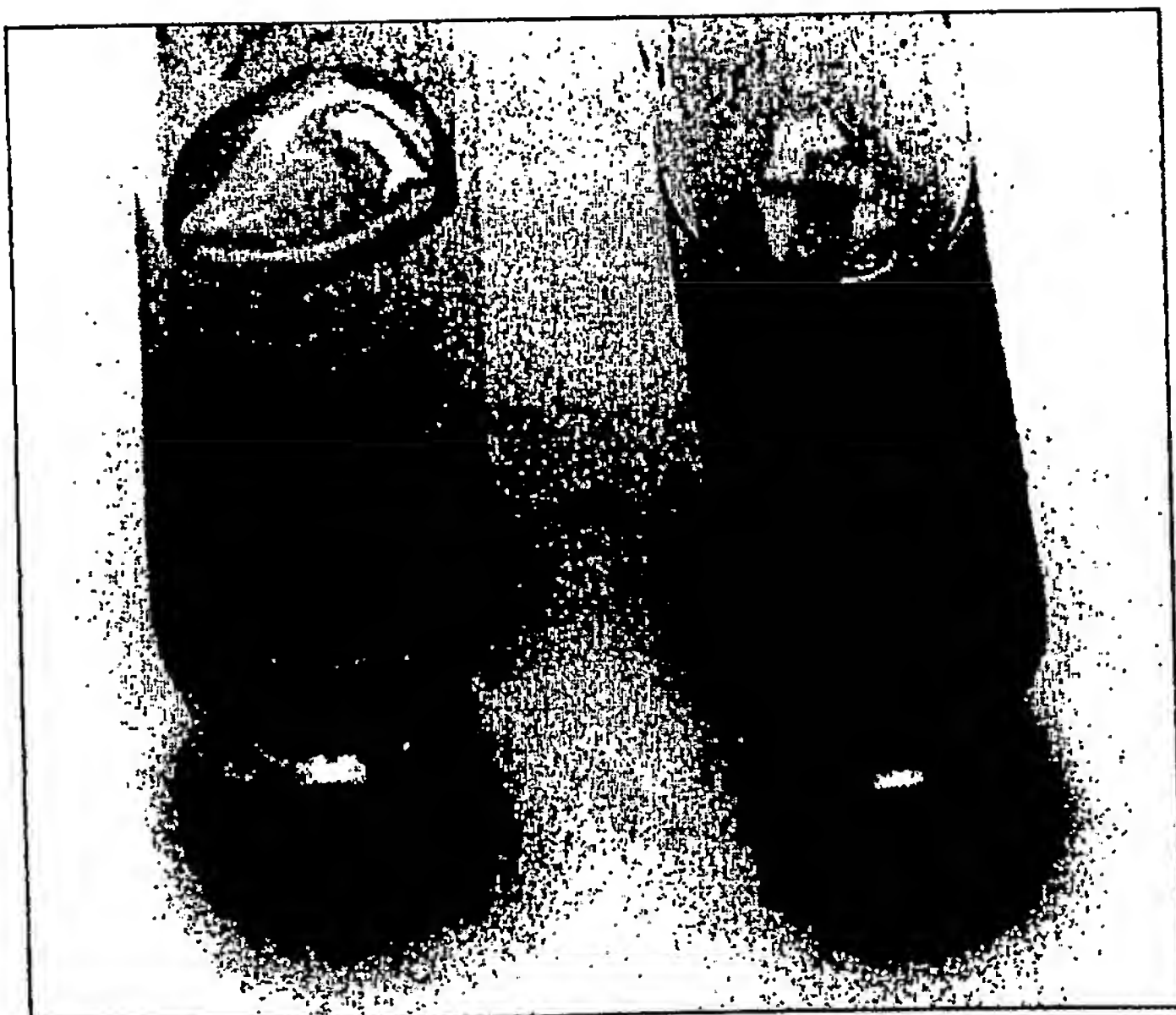


Figure 2b

- 3/6 -

Hexamethyldisiloxane and water

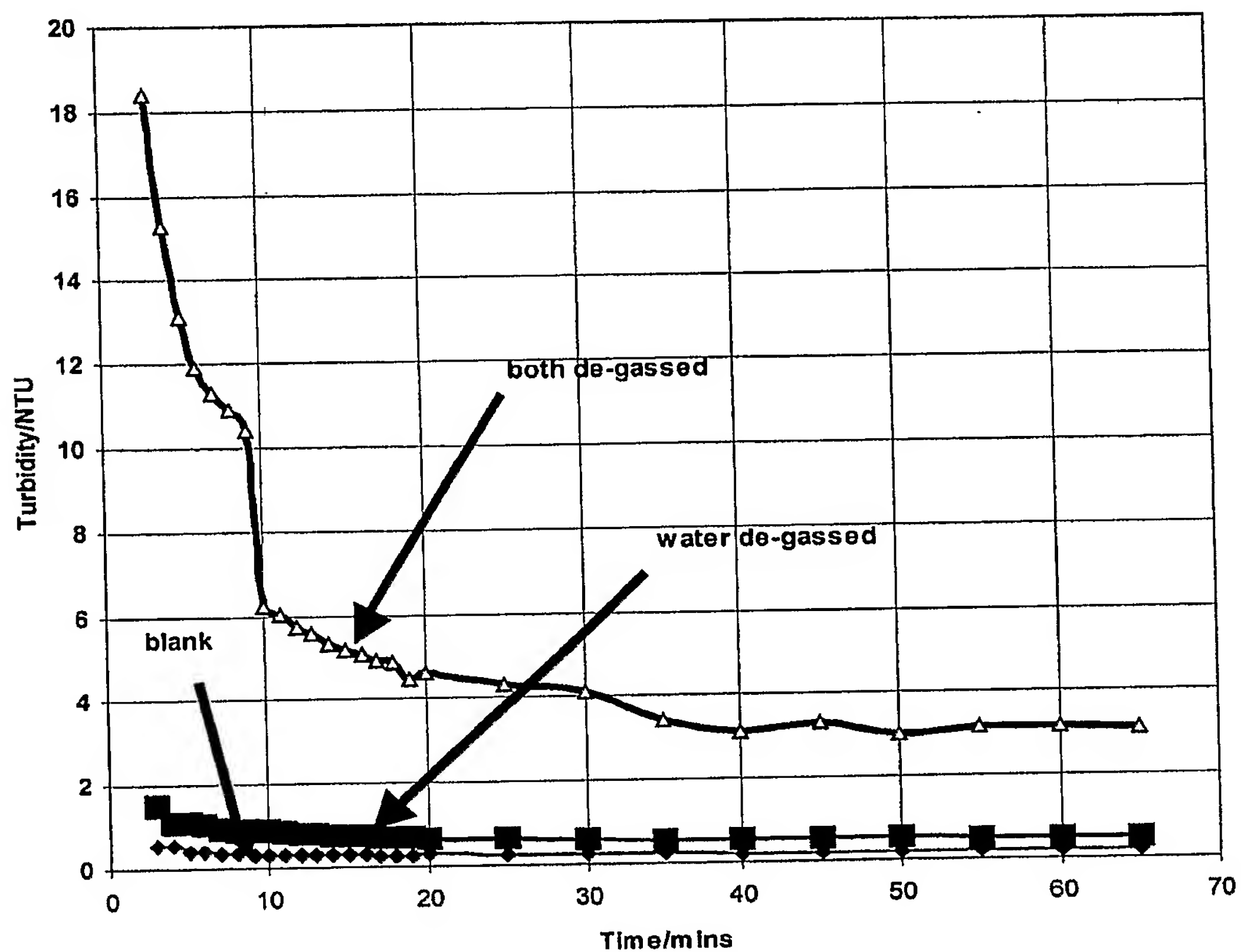


Figure 4

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Perfluorohexane turbidity measurements

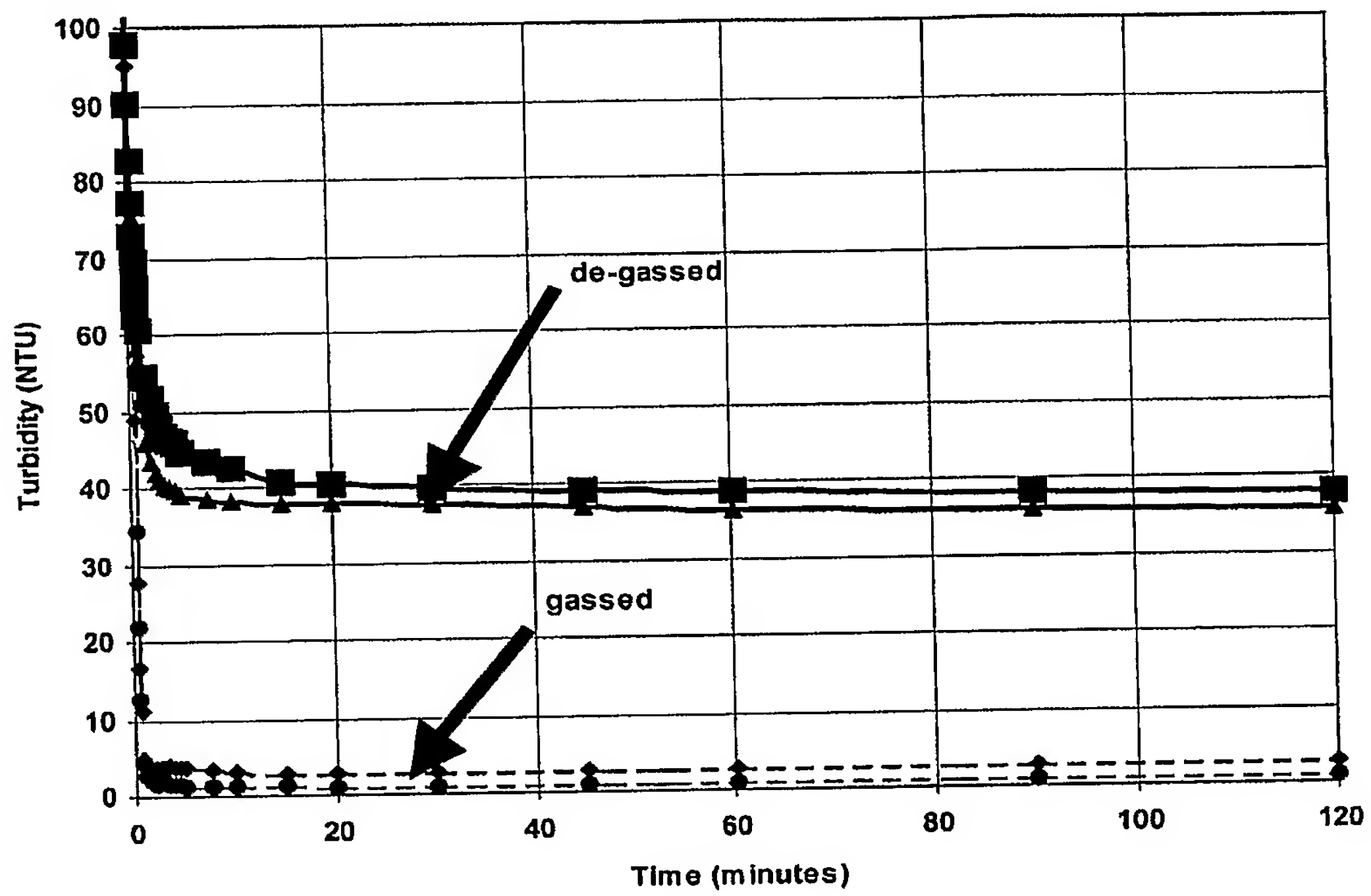
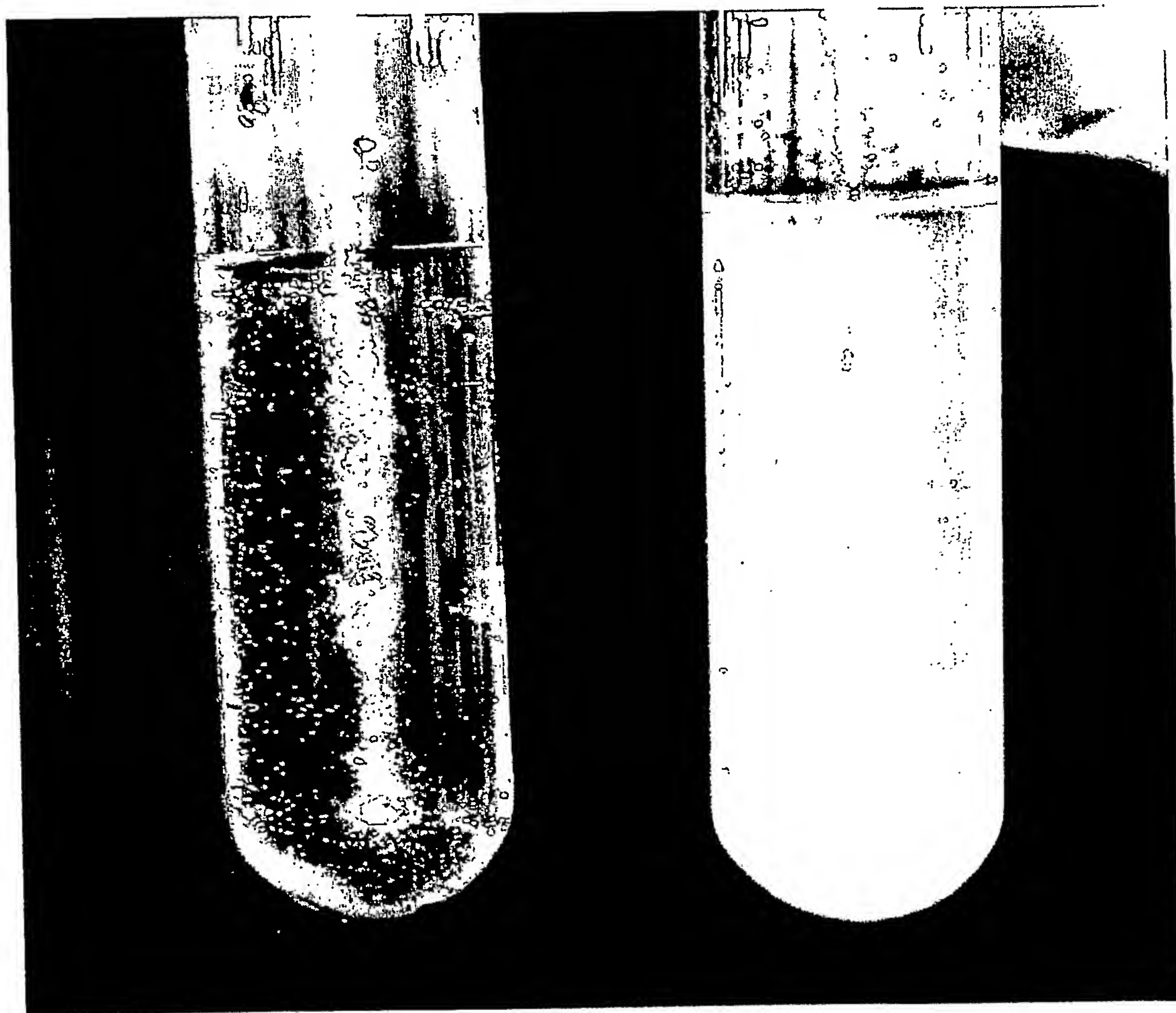


Figure 5

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Perfluorohexane cleaned from a Pyrex tube using gassed water (left) and a combination of de-gassed oil and de-gassed water (right).



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Figure 6

Schematic diagram of a de-gassed water spray cleaning system

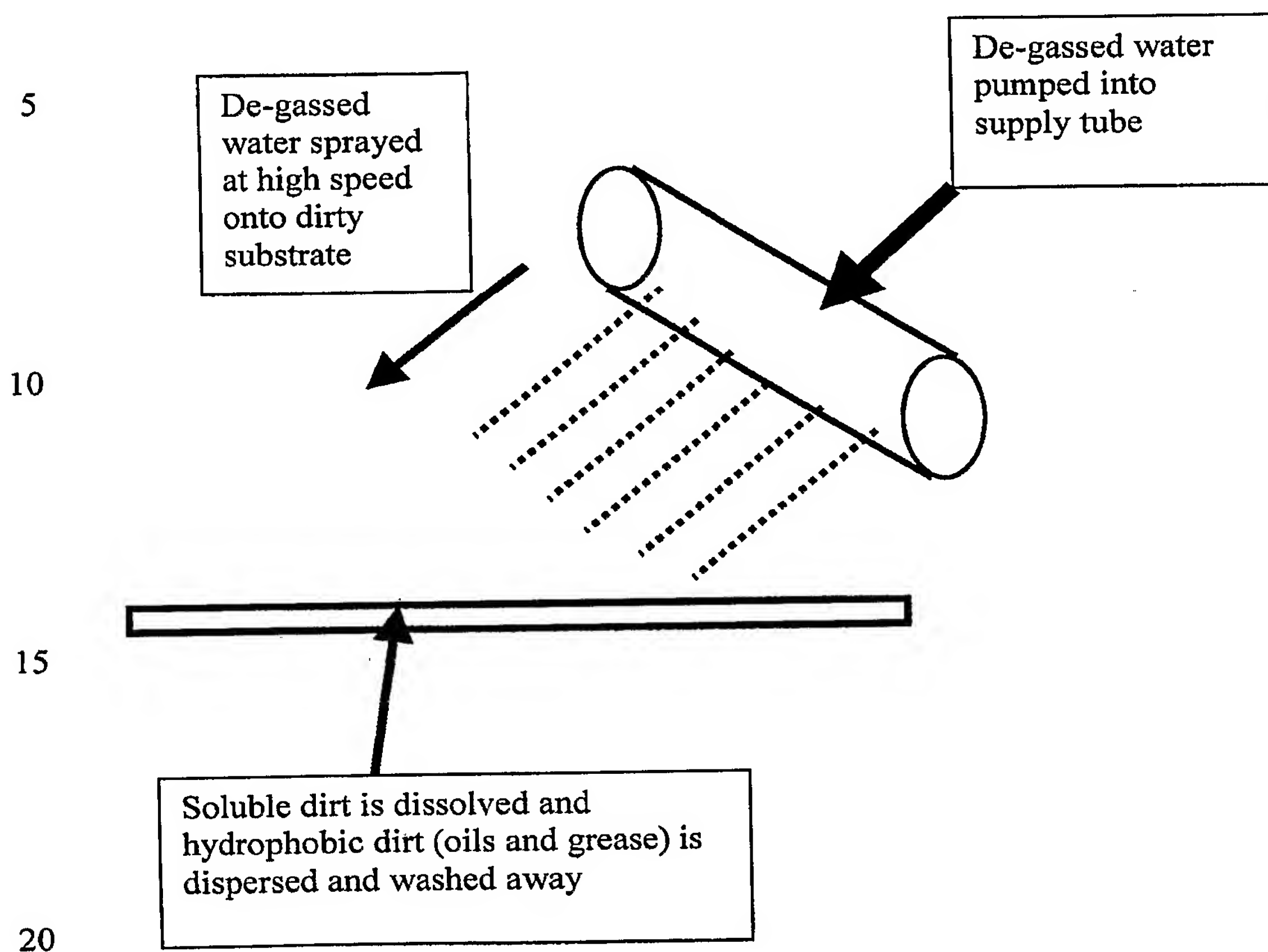


Figure 7